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REACTION OF DIMETHYLAMINOBENZALDEHYDE IN SULFURIC ACID WITH LIQUID OLEFINS

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The analysis of trace quantities of gaseous and vapor state olefins by reaction with dimethylaminobenzaldehyde (DAB) reagent in concentrated sulfuric acid has been reported elsewhere (2). This same reagent also reacts with liquid olefins to form similar products also having strong absorption bands in the 500 mμ region. The liquid olefins have been studied using somewhat different reaction conditions; consequently the positions, shapes, and intensities of the absorption bands differ somewhat from those reported in the vapor phase studies. Although the work done on liquid olefins was not as extensive as in the investigation of olefin gases and vapors (2), the results should have applicability in the identification and analysis of small quantities of liquid olefins.

PROCEDURE

The quantities of liquid olefins used ranged from 0.6 to 20 mg per 100 ml of concentrated sulfuric acid. The olefins were rediluted ten to one and allowed to react in concentrated sulfuric acid for varying times up to two hours, but usually were reacted the full two hour period. The p-dimethylaminobenzaldehyde reagent (10% DAB in glacial acetic acid) was then reacted with the olefin in sulfuric acid for one hour. The DAB reagent and the sulfuric acid usually were mixed in the ratio of one part by volume of DAB

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reagent to eight parts by volume of sulfuric acid. However, various other ratios were used. These included some measurements at a 1:80 ratio of D/B reagent to sulfuric acid, as in the vapor phase investigation. The absorbances of the products were read at 500 mμ usually on a Cary model 11 spectrophotometer. Other details of the experimental procedure are reported elsewhere (1,2).

Absorptivities of Olefins. -- The absorptivities at 500 mμ for ten liquid olefins in the five to eight carbon atom range are given in Table I. The olefins were reacted in concentrated sulfuric acid for two hours, then D/B reagent was added at a ratio of one part of reagent to eight parts by volume of concentrated sulfuric acid, reacted for one hour, and the absorbance read at 500 mμ.

The absorptivities of the five to eight carbon monoolefins range from 0.16 to 0.23 μg^{-1} ml cm^{-1}. The diolefins under these reaction conditions react only slightly to give absorptivities in the 0.016 to 0.039 μg^{-1} ml cm^{-1}. These results contrast sharply with the results obtained with ppm quantities of vapor olefins (2). With the vapors a procedure involving heating of the products formed and use of a 1:80 ratio of DAB reagent to sulfuric acid resulted in absorptivities for the diolefins as high as those of the most reactive monoolefins.

Pure propylene and butene gases when collected under the same conditions as the liquid olefins reported in Table I produce products with absorptivities in the 0.04 to 0.06 μg^{-1} ml cm^{-1}. Ethylene is unreactive. The collection of a pure gaseous olefin is not comparable to the addition of a small amount of liquid to the sulfuric acid. The olefin concentration at the point of diffusion of olefin into the sulfuric acid is quite different.

Measurements of the absorptivity of the 1-hexene product also were made when liquid olefin was added to the reaction mixture used for trace concentrations of vapor. Under these much different reaction conditions an absorptivity of 0.055 μg^{-1} ml cm^{-1} was obtained for the product. Very small amounts of olefin were used in this later work, 0.6 to 20μg per ml of reagent solution. The absorbance was linear with concentration at least in the range from 2 to 20 μg per ml of reagent.

Nature of Absorption Spectra. -- All of the liquid monoolefins react at a 1:8 ratio of DAB reagent to sulfuric acid to form products with maxima at 500 mμ and shoulders at 475 mμ. The conjugated diolefins, 2-methylbutadiene-1,3 and 2,3-dimethylbutadiene-1,3, also form products with maxima at 500 mμ and shoulders at 475 mμ. However, 1,3-pentadiene and 2,5-dimethylhexadiene-1,5 reacted to form products with maxima at 470 mμ and only a shoulder at 500 mμ. The 1,5-hexadiene product did have a maximum at 500 mμ but another weaker maximum appeared at 450 mμ. Consequently, although the absorption bands of the monoolefin products are qualitatively the same, the band systems of the products formed by the diolefins are variable.

Absorptivities of Interfering Substances. -- A considerable number of inorganic and organic substances were reacted under the same conditions as the liquid olefins (Table II). No significant direct reaction with the DAB reagent was found for carbon monoxide, ammonia, nitrogen dioxide, sulfur dioxide, acetylene, benzene, formaldehyde, acetaldehyde, propionaldehyde, crotonaldehyde, acetone, methyl ethyl ketone, ethyl acetate, diethyl ether, sec.-butylamine, aniline, phenol, methyl alcohol or ethyl alcohol. Thiophene and especially propyl and higher alcohols will react vigorously with DAB reagent. Esters and

ethers which will hydrolyze to give higher alcohols in sulfuric acid also should interfere seriously. Higher alcohols (3,5) and esters (4) have been quantitatively determined previously using dimethylaminobenzaldehyde as the colorimetric reagent. Consequently, liquid olefins cannot be determined (by DAB reagent) in liquid mixtures containing higher alcohols, esters or ethers. Sulfur compounds of some types also are likely to interfere significantly.

In addition to interference by direct reaction with the reagent, interference may occur in sulfuric acid medium owing to cross reactions of certain substances with the olefins. Although no measurements were made on such systems under the present experimental conditions, measurements in sulfuric acid alone(1), and extensive measurements with trace quantities of vapor mixtures in DAB reagent (2), indicate serious cross-reactions of formaldehyde, most aromatic hydrocarbons and some phenols with olefins. A number of liquid and solid absorbent systems can be used to remove these interferences from vapor mixtures. However, these methods do not appear to be very convenient for liquid mixtures. Removal of some of these interferences by means of favorable partition ratios for interferences between an aqueous phase and the non-aqueous liquid sample might prove useful.

Effect of Sulfuric Acid Concentration of Absorptivities. -- The absorptivities were measured for the 1-hexene product at various sulfuric acid concentrations. The results were as follows: 97% acid, 0.21; 94% acid, 0.19, 91% acid, 0.17; 86% acid, 0.13 μg^{-1} ml cm^{-1}. At 81% sulfuric acid, no absorption was measurable at 500 mμ. In 91% and 86% sulfuric acid solutions the absorption maximum at 500 mμ shifted down to 480-490 mμ and the resulting absorption band was broadened.

Effect of Ratio of DAB Reagent to Sulfuric Acid on Absorptivities. -- The ratio of DAB reagent to sulfuric acid was varied to determine the ratio giving the highest absorptivities at 500 mμ. Results for 2-methyl-1-butene, 1-hexene and 2-hexene are given in Table III. A 1:8 ratio of DAB reagent solution to sulfuric acid appears optimum.

Reaction Rate of Olefin with DAB Reagent. -- The absorptivities also were determined at various times after the addition of the DAB reagent to the olefin in sulfuric acid solution (Table III). One hour appears to be about the optimum time after addition of the DAB reagent to read the absorbance at 500 mμ. However, only a small loss in absorptivity would result from the use of a 30-minute reaction period.

Reaction Time of Olefin in Sulfuric Acid. -- In the data discussed previously a two hour reaction time of the olefin in sulfuric acid was used. This time was based on the optimum reaction period found in earlier work (1). Later some data also were obtained varying the reaction time in sulfuric acid, but maintaining the reaction time after the addition of DAB at 60 minutes. Measurements made on several liquid olefins indicated that a shorter reaction time in sulfuric acid actually would result in somewhat higher absorptivities. Reaction times of 20 or 30 minutes appear to be acceptable. However, if the DAB reagent is added to the olefin in sulfuric acid immediately after the olefin is dissolved in the acid, a decrease in the absorptivities occurs.

Temperature of Sulfuric Acid Solution. -- If the solution of olefin in sulfuric acid is heated during the period before addition of DAB reagent, a decrease in the absorptivity results. For example, if a solution containing

5 μg per milliliter of 2-methyl-2-butene in sulfuric acid was heated at 100° for 10 minutes after a 50 minute reaction period, the absorptivity decreased from 0.16 to 0.13 μg^{-1} ml cm^{-1}.

DISCUSSION

The products formed by the liquid olefins with D&B reagent absorb about as intensely as do the products formed by vapor phase olefins. Olefin concentrations of 1 μg per milliliter of reagent can be determined quantitatively. The interference situation makes it unlikely that this method should be applied to mixtures containing appreciable quantities of formaldehyde, aromatic compounds or the heterocyclic sulfur compounds. The procedure should have qualitative or quantitative applicability to mixtures of olefins with other aliphatic materials including paraffins, acetylenes, and some types of aldehydes, ketones, esters, ethers and acids.

LITERATURE CITED

1. Altshuller, A.P., Sleva, S.F., Wartburg, A.F., Anal. Chem. 32, 946 (1960).

2. Altshuller, A.P., Sleva, S.F., Anal. Chem. 33 (1961).

3. Coles, H.W., Tournay, W.E., Ind. Eng. Chem. (Anal. Ed.) 14, 20 (1942).

4. Custance, H.N., Huggins, M., Analyst 74, 310 (1949).

5. Penniman, W.B.D., Smith, D.C., Lawshe, E. I., Ind. Eng. Chem. (Anal. Ed.) 9, 91 (1937).

Symposium on Air Pollution, Joint with Division of Petroleum Chemistry, 136th Meeting, ACS, Atlantic City, New Jersey, 1959.

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TABLE I. ABSORPTIVITIES FOR THE PRODUCTS OF LIQUID OLEFINS WITH p-DIMETHYLAMINOBENZALDEHYDE REAGENT

Olefin	Absorptivites at 500 mμ μg^{-1} ml cm^{-1}
1-pentene	0.18±0.02 [a]
2-methyl-1-butene	0.18±0.005
2-methyl-2-butene	0.19±0.01
2-methyl-1,3-butadiene	0.016±0.002
1-hexene	0.21±0.015
2-hexene	0.19±0.015
4-methyl-trans-2-pentene	0.16±0.015
1,5-hexadiene	0.039±0.005
2,4,4-trimethyl-1-pentene	0.23±0.015
2,5-dimethyl-1,5-hexadiene	0.024±0.004

[a] one standard deviation

TABLE II. ABSORPTIVITIES FOR THE PRODUCTS OF VARIOUS INORGANIC AND ORGANIC SUBSTANCES WITH p-DIMETHYLAMINOBENZALDEHYDE REAGENT

Substance	Absorptivity at 500 mμ μg^{-1} ml cm^{-1}
carbon monoxide	$< 10^{-6}$
ammonia	$< 10^{-6}$
nitrogen dioxide	$< 10^{-6}$
sulfur dioxide	$< 10^{-6}$
acetylene	0.00002
benzene	0.00003
formaldehyde	$< 10^{-6}$
acetaldehyde	0.0003
propionaldehyde	0.003
crotonaldehyde	0.0005
acetone	0.0001
methylethyl ketone	0.002
ethyl acetate	0.00002
diethyl ether	0.00008
sec.-butylamine	0.000006
aniline	0.00001
phenol	0.000007
thiophene	0.02
methyl alcohol	0.000006
ethyl alcohol	0.0003

Table II cont.

Substance	Absorptivity at 500 mμ μg-1 ml cm-1
n-propanol	0.040±0.01 [a]
iso-propanol	0.033±0.01
n-butanol	0.19±0.06
t-butanol	0.11±0.03
iso-pentanol	0.22±0.02

[a] one standard deviation

TABLE III. EFFECT OF REACTION TIME AND RATIO OF DAB REAGENT TO SULFURIC ACID ON THE ABSORPTIVITIES OF OLEFIN PRODUCTS

Olefin	Time, minutes	Absorptivities at 500 mμ at various ratios of DAB reagent to sulfuric acid, μg^{-1} ml cm^{-1}. 1 to 8 ratio	1 to 4 ratio	3 to 8 ratio,
2-methyl-1-butene	5	0.10	0.14	---
	30	0.16	0.13	
	60	0.17	0.12	
	85	0.16		
1-hexene	15	0.14	0.17	0.12
	35	0.18	0.17	0.11
	60	0.20	---	---
	90	---	0.10	---
	110	0.12	---	---
2-hexene	10	0.10	0.11	0.08
	30	0.13	0.11	---
	60	0.16	0.11	0.08
	90	0.16	---	---